Temperature dependence of the spin and orbital magnetization density in $Sm_{1-x}Gd_xAl_2$ around the spin-orbital compensation point.

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Non-resonant ferromagnetic x-ray diffraction has been used to separate the spin and orbital contribution to the magnetization density of the proposed zero-moment ferromagnet $Sm_{0.982}Gd_{0.018}Al_2$. The alignment of the spin and orbital moments relative to the net magnetization shows a sign reversal at 84K, the compensation temperature. Below this temperature the orbital moment is larger than the spin moment, and vice versa above it. This result implies that the compensation mechanism is driven by the different temperature dependencies of the $4f$ spin and orbital moments. Specific heat data indicate that the system remains ferromagnetically ordered throughout.

Recently, it was proposed that the Laves phase compound $Sm_{1-x}Gd_xAl_2$ exhibits a spin-orbital compensation point at $\approx 85K$ when x = 0.0185 [1]. Magnetometery showed that the net moment dipped to zero at this temperature, but was finite either side in the magnetically ordered phase (the Curie temperature is 128K). At the compensation temperature, magnetic Compton scattering shows a net *spin* moment, indicating that the system consists of a ferromagnetically ordered spin sublattice[2]. For the net moment to be zero, this spin moment must be exactly compensated by the orbital moment. Although it is thought that this may be driven by the different temperature dependencies of the Sm $4f$ spin and orbital moments, this had not yet been investigated. An understanding of the compensation mechanism may be gained by studying the temperature dependence of the spin and orbital moments near the compensation point, which requires direct measurement of the spin and orbital magnetization. Such an x-ray diffraction study is reported here for the first time. Our result conclusively proves that the compensation point is driven by the different temperature dependence of the spin and the orbital moments. Our specific heat data indicate that the system remains magnetically ordered.

The magnetism of Sm and its compounds has been the focus of many investigations as a result of the importance of the conduction electron polarization and the complex crystalline electric field (CEF) in the material[3]. The spin and orbital contribution to the Sm^{3+} $4f$ moment are of similar size and aligned antiparallel, and the polarized conduction electron spin moment is thought to align parallel with the $4f$ spin moment[4]. The three components to the site magnetization almost cancel, leaving a small net local moment. Interestingly, the temperature dependencies of the spin and orbital components are not identical due to a complex thermal admixture of nearly degenerate **J** multiplets in which the Sm^{3+} ion exists in (the ground state 5/2 muliplet is 1500K from first excited state 7/2). The admixture arises from the CEF effect on the degeneracy of the **J** states and has long been an explanation of the magnetism in Sm compounds [5].

A solid solution of Gd^{3+}, introduces a large (7.6 μ_B) spin moment onto the Sm site in $Sm_{1-x}Gd_xAl_2$ and the small induced lattice distortion alters the CEF deformation potential. It also critically affects the RKKY exchange interaction due to the increase in conduction electron polarization. These factors have a considerable influence on the temperature dependence of the Sm site moment, as the thermal admixture of **J** states is renormalized. The result is to change the temperature dependencies of the $4f$ spin and orbital moments. In the undoped compound the moments are $M_l \approx 4.3\mu_B$ and $M_s \approx -3.8\mu_B$ [6] respectively. The change in the CEF allows the Sm orbital and Gd/Sm spin contributions to cancel each other completely at a distinct temperature below T_C: at this point the material has no net moment, and is referred to as compensated. This effect in itself is not unusual in some ferrimagnetic systems, where *two* sublattice magnetizations become equal and opposite at a particular temperature. However in this case the magnetism exists only on the rare earth site (a solid solution of Sm / Gd ions). A naive picture of the temperature dependence has three order parameters, $4f$ orbital magnetism, $4f$ spin magnetism, and conduction electron spin polarization with the latter probably having the same temperature dependence as that of the $4f$ spin. If the order parameters are of opposite sign, with non-identical temperature dependence the system can become compensated. Previous work has concentrated on the bulk magnetization and the type of magnetic ordering at the compensation point. However the mechanism of compensation in $Sm_{1-x}Gd_xAl_2$ has not been investigated.

In this letter we report the use of non-resonant x-ray diffraction to investigate the magnetization density of $Sm_{0.98}Gd_{0.012}Al_2$ as a function of temperature through the spin-orbital compensation point by monitoring a Bragg reflection. The technique has the advantage of allowing the separation of the spin and orbital form factors by changing the experimental geometry. At the wavevector sampled, the conduction electron moment makes

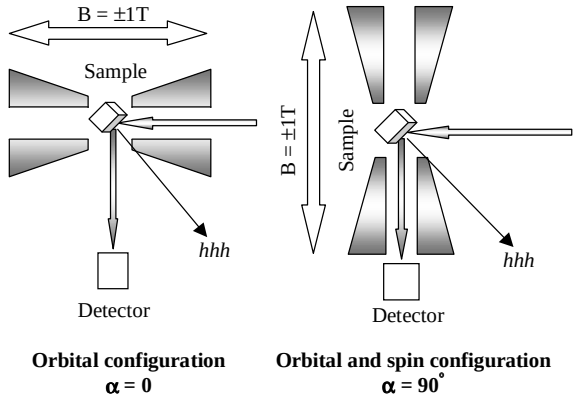

FIG. 1: Schematic layout of a generic non-resonant ferromagnetic diffraction experiment. Left hand figure shows experimental configuration for measurement of the orbital component of the form factor. Right hand figure shows configuration for measurement of the total (L+S) form factor.

no contribution to the form factor, therefore the technique gives direct access to the temperature dependence of the spin and orbital components of the $4f$ moment.

This is the first direct observation of the temperature dependence of the $4f$ spin and orbital form factors. From our investigation it is clear that the conduction electron polarization is a critical factor in the compensation process as, at $T > T_{comp}$, the $4f$ moments remain almost compensated. From our own investigation of the bulk properties of the material, in particular the magnetic contribution to the specific heat, presented later, it is clear that at the compensation point the material exhibits no change in entropy, and therefore does not exhibit any sign of a magnetic transition. This is due, in part, to the high anisotropy in the system.

The technique of non-resonant x-ray diffraction has recently been developed as a convenient method of studying the spin density in ferromagnetic materials using elliptically polarized synchrotron radiation. It is particularly useful for materials where the neutron technique is not viable due to the high neutron absorption cross section. The technique also gives a convenient method of separating the spin and the orbital contribution to the total magnetic form factor by changing the experimental geometry (see fig 1). Essentially the technique makes use of the suppression of Thompson charge scattering at a scattering angle of 90° for radiation linearly polarized in the scattering plane. When elliptically polarized photons are incident, the charge and magnetic Bragg intensities interfere. This leads to modulation of the signal with reversal of the sign of magnetic component, this can be achieved by either flipping the sample magnetization vector (in the scattering plane), or by flipping the helicity of the incident beam polarization. When the pure charge scattering is a minimum, the signal modulation, resulting from the magnetic scattering cross section, tends to a maximum, which facilitates the measurement of a flipping ratio.

The fractional change in intensity upon reversal of the sample magnetization or the photon helicity is related to the orbital (F_L), spin (F_S) and charge(F_C) form factors as:

$$R(\alpha) = \frac{I_\uparrow - I_\downarrow}{I_\uparrow + I_\downarrow} = g f_p \frac{2F_S(\mathbf{k})sin\alpha + F_L(\mathbf{k})(sin\alpha + cos\alpha)}{F_C(\mathbf{k})} \tag{1}$$

where $g = \hbar\omega/m_e c^2$, $f_p = P_c/(1 - P_l)$, P_c and P_l are parameters for the circular and linear component of the beam, and thus describe the degree of ellipticity of the incident photons.

The orbital and spin contributions to the form factor are defined in terms of α the angle between the B field and the incident beam (see fig 1):

$$R(\alpha = 0) = -2 g f_p \frac{F_L}{F_C} \tag{2}$$

$$R(\alpha = 90^\circ) = -2 g f_p \frac{F_S + F_L}{F_C} \tag{3}$$

In the past most experiments have made use of a polychromatic incident beam of x-rays, in order to collect data on a number of Bragg peaks simultaneously, using energy dispersive Ge detectors. However, the white beam method suffers from multiple diffraction which corrupts the signal and is difficult to model. In this investigation a monochromatic beam was used to avoid these uncertainties. However the principle remains identical to that described previously for white beam experiments[7],[8].

A single crystal sample of $Sm_{1-x}Gd_xAl_2$ with $x = 0.018$ was produced by the Bridgemann method, with the polycrystalline boule sealed in a Ta can to maintain stoichiometry. The structure of the resulting crystal was verified as the C_{15} Laves phase using Laue photography.

The non resonant magnetic diffraction experiment was performed on the XMaS beamline[9] at ESRF. Elliptically polarized radiation was extracted by viewing the bending magnet source at a angle of $\approx$ 0.3mrad from the plane of the synchrotron: the optimum position in terms of signal to noise. The sample was mounted in a Be shrouded closed cycle He cryostat. An incident energy of 5.736keV was selected using the double bounce Si monochromator, such that the 333 reflection was in the Bragg condition with a scattering angle of 90° in the plane of the synchrotron (see fig 1). The calculated polarization of the beam at the incident energy used was $P_l = 0.99470$ and $P_c = -0.02937$ [10], yielding a polarization factor, f_p, of -5.5. The diffracted beam was detected using a fast NaI scintillator with an average count

rate of ≈ 85000cps at the diffraction peak. The magnetic field was applied using a 1T electromagnet, which was flipped at intervals of 20s in order to average over the beam position fluctuations inherent with the bending magnet source. In this configuration a single flipping ratio was acquired over an integration time of 2hours. The flipping ratios of the 333 reflection were measured as a function of temperature, in the total (eq 3) moment configuration and the orbital only (eq 2) configuration, in both heating and cooling cycles to ensure reproducibility of the data. At $sin\theta/\lambda = 0.32\mathring{A}^{-1}$ on the form factor curve only the $4f$ moments contribute to the magnetic signal.

A comprehensive investigation of the magnetic properties of the sample was performed at Warwick University using SQUID and VSM magnetometery, specific heat measurements and AC susceptibility, in order to check sample quality and to investigate the complex magnetic properties of the sample comprehensively.

For reflections of the type hhh where h is odd, only the $4f$ site contributes to the phase factor. The temperature dependence of the orbital, spin and total form factor curve at $sin\theta/\lambda = 0.32\mathring{A}^{-1}$ is shown in fig 2. It is clear that below the compensation temperature the orbital contribution is positive (fig 2 A), and thus the derived spin contribution is negative (fig 2 B), with a smaller magnitude as expected, since at this wave vector the conduction electron polarization is not measured. The spin-only form factor result is in good agreement with that measured previously for the un-doped sample[11]. Above the compensation temperature the spin and orbital contributions are reversed, with approximately equal magnitudes. The total form factor (fig 2 C) is positive below the compensation temperature, as expected, since the total magnetization will follow the large orbital contribution. Interestingly above T_{comp} the total form factor is negligible. It is clear that both the orbital and the spin component to the form factor have a complex temperature dependence, furthermore both components flip sign at T_{comp}, with the total form factor tending to zero at T_{comp}. This result implies that the systems exhibits no ferro-magnetic character at T_{comp}. This does not mean that the system becomes paramagnetic however, or that the orbital, or spin magnetizations disappear at the compensation point, for the following reasons.

The orbital and spin components to the magnetization have different temperature dependence and an anti-parallel arrangement. The net moment in the system will always align with the field, (when the field is large i.e. 1T see next section). At low temperature this results in a positive contribution to the magnetization density arising from the orbital moment and a negative contribution arising from the spin moment, with a net positive magnetization density where L>S. When the system becomes compensated the orbital and spin components are in effect antiferro-magnetically aligned. However the orbital

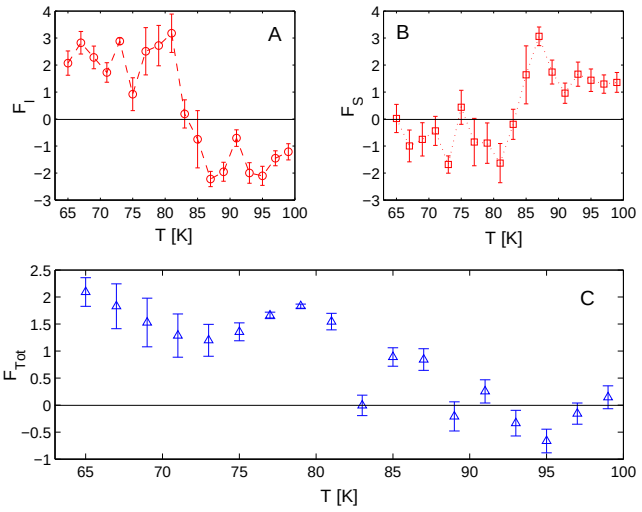

FIG. 2: Temperature dependence of the flipping ratio of the 333 reflection for $Sm_{1-x}Gd_xAl_2$. **A**: Orbital only form factor temperature dependence (Circle). **B**: Derived spin form factor temperature dependence(Square). **C**: Temperature dependence of the total form factor (Triangle).

and the spin components should still be finite. Our data show a definite sign reversal of the spin and the orbital components. The change of sign results from the spin component becoming dominant above T_{comp}, hence the net moment is re-aligned with respect to the field.

The fact that our orbital data tend to zero smoothly at T_{comp} rather than exhibiting a sharp step-like transition, is a statistical artefact produced from a combination of unwanted beam movements, from the synchrotron bending magnet source, and temperature fluctuations in the cryostat due to reversing the applied field. If one assumes that the temperature is only stable to within $\pm 0.5K$ one may easily reach a point whereby the sample is driven from one side of T_{comp} to the other, by the eddy current heating effect, throughout the period of the measurement, thereby measuring zero.

Above T_{comp} the measured form factor is negligible. This means that the $4f$ components to the magnetization are of a similar size, which in turn implies that the conduction electron spin component (not measured by the diffraction experiment) is of critical importance. Our diffraction data provide clear evidence that the spin and the orbital contributions to the $4f$ magnetization density cancel at the compensation point, and that the compensation point occurs as a result of the different temperature dependence of the spin and orbital form factor.

This diffraction result will now be discussed in the context of the bulk properties of the system. Firstly the magnetization data observed for the sample as a function of temperature (fig 3:A). The bulk magnetization data clearly show that, at the compensation point, the net moment in the sample is zero. However the magnetic behav-

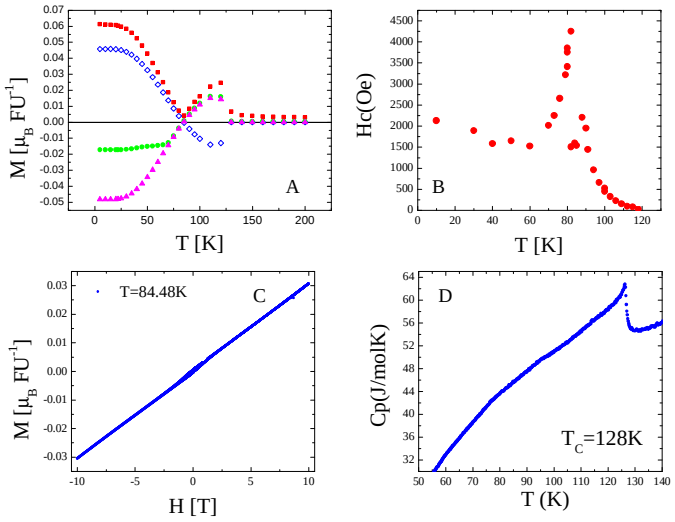

FIG. 3: Low temperature properties of $Sm_{1-x}Gd_xAl_2$. **A**: Magnetization as a function of temperature. Triangles Field cooled in 10^{-2}T. Circles field cooled in 0.1T. Diamonds zero field cooled. Squares field cooled in 1T. **B**: Temperature dependence of the coercive field. **C**: Magnetization as a function of field (up to 10 T) at T_{comp}. **D**: Specific heat capacity.

ior below T_{comp} drastically alters, depending on whether the sample is field cooled or zero field cooled. On cooling in a small 10^{-2}T field the magnetization shows a large diamagnetic effect below T_{comp} (fig 3:A, triangles). The size of the diamagnetic effect can be altered by changing the magnitude of the applied field (fig 3:A, 0.1T (circles) and 1T (squares)). If the system in first field cooled and then warmed through T_{comp} in the remnant field the system again shows some diamagnetic effect.

This is an effect of the large anisotropy within the system. The Sm $4f$ moment can be thought of as a single site ferri-magnet, with the spin and orbital contributions having different temperature dependencies if the size of each contribution is reversed either side of T_{comp} the system must overcome the magnetocrystalline anisotropy energy (MAE) to realign the net moment with the applied (or remnant) field as is observed in the diffraction experiment. It follows that if $\mu.B < MAE$ the system exhibits a large diamagnetic effect. The strong MAE effect in this system is demonstrated by the temperature dependence of the coercive field (fig 3:B) which clearly shows maxima above and below T_{comp}. When considered with the diffraction data the behavior of the magnetic system is clarified. The diffraction data were taken in an applied field of 1T, which is large enough to overcome the large MAE and hence realign the net moment in the system. The closed hysteresis loop at T_{comp} (fig 3:C) is verification that the system is compensated and indicating a strongly correlated quasi anti-ferromagnetic behavior

The specific heat capacity (fig 3:D) shows a large λ-type anomaly associated with the Curie temperature at T_c=128K, however there is no effect in the specific heat data at a temperature corresponding to T_{comp} which indicates that there is no transition at that temperature.

It is obvious that the conduction electron moment is an important factor in the magnetization in this material. The alloying of 2% Gd will certainly affect the RKKY polarization in the system due to the lattice distortion and also the large size of the Gd moment. It is also clear that the $4f$ contributions above T_{comp} appear, from our data to be equal. Thus it is reasonable to assume that the net magnetization observed above T_{comp} (fig 3:A) results almost exclusively from the conduction electron moment in the system, the temperature dependence of which is unknown (although it is reasonable to assume it is similar to the $4f$ spin moment) Such a measurement is planned using the magnetic Compton scattering technique, which directly samples the polarization of all spin polarized electrons.

In conclusion, our data show that the total $4f$ magnetization density is zero at the compensation temperature. We have demonstrated that the compensation mechanism is driven by the temperature dependence of the spin and orbital moments in the system. We have shown that the unusual temperature dependence of the bulk magnetization is driven by the reversal of the dominant $4f$ component at the compensation temperature, i.e. $T < T_{comp}$:L>S and $T > T_{comp}$:S>L. The fact the bulk measurement of specific heat shows no anomaly at the T_{comp} implies that magnetic system remains ordered, as one may expect due to the high magnetocrystalline anisotropy energy.

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